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EFFECT OF SILICON ON THE INTERGRANULAR CORROSION AND GRAIN-BOUNDARY ENERGY OF AUSTENITIC NICKEL-CHROMIUM STAINLESS STEELS

A. Camus, A. Desestret, M. Froment and P. Guiraldenq

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A. Camus, A. Desestret, M. Froment and P. Guiraldenq.

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16. Abstract
Addition of 1% silicon to the austenitic nickel-chromium steels produces a maximum in grain-boundary energy and a corresponding maximum in sensitivity to intergranular corrosion. Quenched austenitic nickel-chromium stainless steels undergo intergranular corrosion when they are held at high anodic potentials corresponding to the transpassivity region. Addition of silicon to these steels produces a considerable change in the magnitude of this type of corrosion: holding specimens in the transpassivity region by means of a potentiostat and immersion in nitric acid containing hexavalent chromium both show maximum intergranular attack on steels containing around 1% silicon; above 2% silicon the intergranular attack disappears completely.

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EFFECT OF SILICON ON THE INTERGRANULAR CORROSION AND GRAIN-BOUNDARY ENERGY OF AUSTENITIC NICKEL-CHROMIUM STAINLESS STEELS

Agnes Camus, Andre Desestret, Michel Froment, and Pierre Guiraldenq

Presented by M. Jean Wyart* /425**

Addition of 1% silicon to the austenitic nickel-chromium steels produces a maximum in grain-boundary energy and a corresponding maximum in sensitivity to intergranular corrosion. Quenched austenitic nickel-chromium stainless steels undergo intergranular corrosion when they are held at high anodic potentials corresponding to the transpassivity region [1, 2]. Addition of silicon to these steels produces a considerable change in the magnitude of this type of corrosion: holding specimens in the transpassivity region by means of a potentiostat [2] and immersion in nitric acid containing hexavalent chromium [3] both show maximum intergranular attack on steels containing around 1% silicon; above 2% silicon the intergranular attack disappears completely.

Electron microscopic observations prove that this intergranular corrosion is not due to preferential attack of one phase, but rather corresponds to different rates of solution of the austenitic matrix near the grain boundaries [4]. In addition, M. A. Streicher [5] has shown that addition of silicon to

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austenitic nickel-chromium steels changes the appearance of the grain boundaries after thermal etching. One may thus assume that silicon has an effect on the grain-boundary energy. To try to verify this hypothesis, in this note we shall discuss in more detail the similarities between thermal etching and electrolytic etching of stainless steels having various silicon contents. Using replicas in the electron microscope, we shall compare the appearances of the intergranular grooves after potentiostatic attack and after thermal attack.

Table I shows the composition of the steels prepared at the Research Center of the Compagnie des Ateliers et Forges de la Loire, using selected starting materials.

The samples were cylinders 10 mm long by 5 mm in diameter; they were first polished mechanically, then electrolytically.

The electrolytic attack consisted of holding the specimen at 1.1 V with respect to the saturated calomel electrode in a 2 N sulfuric acid solution. Electrolysis was limited to a right section of the cylinder, and the quantity of electricity was fixed/ 426 at 1.4 coulombs for all experiments. Thermal etching was carried out by enclosing the specimens in one compartment of a quartz ampoule which contained chips of zirconium-titanium alloy in the other. The ampoule was filled with commercially-pure argon so that it would have a pressure above 1 atm at the holding temperature (1000° C). Preliminary tests showed that treatment for 72 hours would produce sufficient thermal etching (average grain size: 100 μm).

After treatment, carbon replicas were prepared and observed in the electron microscope. Thermal etching leads to determination of the grain-boundary energy if the angle θ of the intergranular groove is known. To measure it, we used the capabilities offered

TABLE I *

C.	Mn.	Si.	S.	P.	Ni.	Cr.
0,013	0,19	0,06	0,009	0,016	13,9	16,1
0,013	0,22	0,12	0,008	0,013	14,0	15,9
0,009	0,23	0,41	0,009	0,016	14,1	16,0
0,008	0,23	0,94	0,008	0,014	13,8	16,4
0,009	0,20	1,32	0,007	0,016	13,8	16,4
0,011	0,24	1,99	0,007	0,014	13,9	16,5
0,011	0,40	3,30	0,011	0,014	15,0	17,0
0,020	0,25	4,35	0,007	0,015	14,7	16,4
0,013	0,29	5,72	0,009	0,016	15,2	16,8

* Translator's note: Commas in numbers represent decimal points.

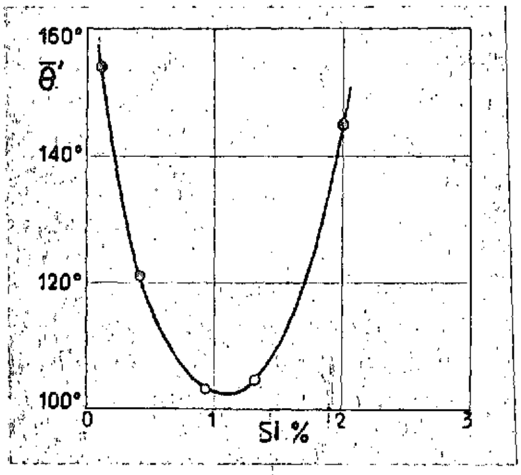

Figure 1. Electrolytic attack: changes, as a function of silicon content, in the angle θ' formed by the intergranular groove, after holding potentiostatically at 1.1V/SCE.

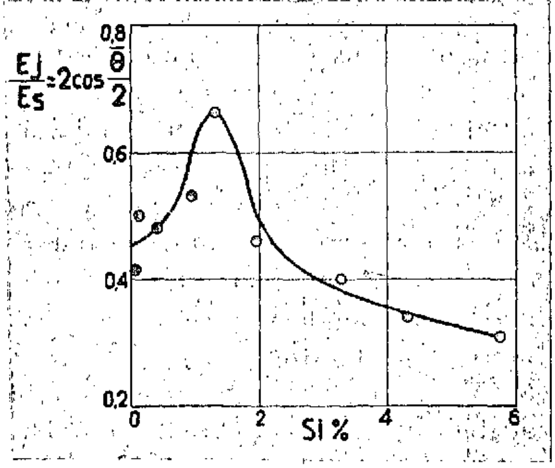

Figure 2. Thermal attack: variation of the ratio of grain-boundary energy E_{gb} to surface energy E_s as a function of silicon content.

TABLE II *

	Silicon content (%)								
	0,06.	0,12.	0,41.	0,94.	1,32.	1,99.	3,30.	4,35.	5,72.
Intergranular groove angle θ (degrees).................	156	151	152	149	141	153	157	160	162
Number of measurements n...	19	35	38	37	27	30	15	15	18
95% confidence interval Δθ (degrees)	6	5	4	4	5	4	5	4	4

* Translator's note: Commas in numbers represent decimal points.

by stereoscopic pairs of micrographs [6]: two photographs of the same grain boundary aligned in the direction of the stereoscopic /427 base line are taken successively, with the object being inclined ±7° with respect to the plane perpendicular to the optic axis of the microscope [7]. In the same way, we have measured the angle θ' of the intergranular groove after potentiostatic corrosion in the sulfuric acid solution.

In Figure 1 are plotted the average values of θ', calculated from at least 12 measurements on each type of steel; measurement of θ' is difficult when the silicon content is less than 0.12% or greater than 1.99%. We can, however, say that these angles are larger than those for the steels containing 0.12 and 1.99% silicon. Figure 1 shows that the dihedral angle θ' of the electrolytic etch-groove passes through a minimum when the silicon content is about 1%; it is known that this content produces maximum intergranular corrosion [2, 3].

We have found that silicon also changes the angle θ of the intergranular groove which appears after thermal attack. Table II shows the change in the average values of θ as a function of silicon content. We also show in this table the number n of measurements made for each steel and the 5% confidence limits $\Delta\theta$.

These data show that the angle θ passes through a minimum for a silicon content of 1.32%. Now, the dihedral angle θ of the thermal etch-groove depends on the grain-boundary energy E_{gb} according to the equation

$$2 \cos \frac{\theta}{2} = \frac{E_{gb}}{E_s},$$

where E_s is the surface energy [8].

Complementary experiments have shown that silicon does not change the surface energy E_s.

Silicon thus has an effect only of the grain-boundary energy E_{gb}, which is a maximum near 1% silicon, as shown in Figure 2 where the values of 2 cos (θ/2) calculated from the results of Table II are graphed. / 428

Figure 2 also shows that the values of the ratio E_{gb}/E_s are smaller at higher silicon contents. This would explain why the steel specimens containing more than 2% silicon are no longer subject to intergranular penetration on being held in nitric acid containing hexavalent chromium. In contrast, the steel specimens containing less than 1% remain sensitive to this type of corrosion [3].

REFERENCES

1. Epelboin, I, M. Froment and Ph. Morel. Corrosion Anticorrosion, Vol. 8, 1960, p. 383.

2. Desestret, A. Thesis, Paris, 1964. Published by the Cercle d'Études des Métaux de Saint-Étienne , [Saint-Etienne Metal-Study Club].

3. Coriou, H., A. Desestret, C. Grall and J. Hochmann. Comptes rendus, Vol. 254, 1962, p. 4467 and Mém. Scient. Rev. Mét. Vol. 61, 1964, p. 177.

4. Desestret, A. and M. Froment. Mém. Scient. Rev. Mét. Vol. 62, 1965, p. 135.

5. Streicher, M. A. J. Electrochem. Soc. Vol. 103, 1956, p. 375.

6. Marraud, A. Bull. Soc. franç. de Photogrammétrie, No. 7, p. 7.

7. Camus, A. Diplôme d'Études supérieures, Paris, 1966.

8. Herring, C. Structure and Properties of Solid Surfaces, Chicago Press, 1952.

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